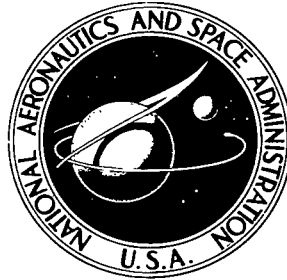


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**DEVELOPABLE IMAGES PRODUCED
BY X-RAYS USING THE NICKEL
HYPOPHOSPHITE SYSTEM**

I — X-Ray Sensitive Salts

*by Charles E. May, Warren H. Philipp,
and Stanley J. Marsik*

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SUMMARY

Twenty-eight crystalline salts were X-irradiated and treated with an ammoniacal nickel hypophosphite solution. Treatment (development) of six of the salts resulted in precipitation of nickel metal. The developable salts were four hypophosphites, sodium phosphite, and nickel formate. We propose a mechanism for the process based on the postulate that micro amounts of hydrogen atoms are formed during the radiation step. During development, these hydrogen atoms cause the formation of nucleation sites of nickel metal. In turn, these sites catalyze further reduction of the nickel cations by the hypophosphite. The results are discussed in terms of application of the process to the formation of developable latent images.

INTRODUCTION

Current research at Lewis Research Center has led to the discovery of a photographic type process based on nickel (ref. 1). It resembled the common silver photographic process in that a latent image formed by radiation could be amplified by development to produce a visible image of wide tonal gradation in the gray scale. Our photographic emulsions contained nickel hypophosphite, and although they were not sensitive to visible light, they were sensitive to X-rays and electron radiation. This lack of sensitivity to visible light can be a distinct advantage in radiography and diffraction in that special light-proof cassettes and darkrooms are not necessary. A second advantage is that relatively more abundant and less expensive nickel replaces the more costly silver in the conventional photographic emulsions.

As yet, the nickel hypophosphite emulsion is not nearly as sensitive as conventional photographic material to X-rays. The exposure time for a good nickel image is about

5 minutes at about 20 000 roentgens per minute using a tungsten target X-ray tube at 250 kilovolts. To make our emulsions more sensitive requires additional research.

This report presents the results of an investigation aimed at finding salts, other than nickel hypophosphite, which produce developable latent images when exposed to X-rays. In addition to a variety of nickel salts, several hypophosphites and salts prone to radiation-induced crystal defects were tested. For simplicity, the crystalline salts were used rather than emulsions; an aqueous nickel hypophosphite solution was used as the developer; and the yield of nickel metal was determined gravimetrically. The discovery of other 'X-ray sensitive' salts has allowed a mechanism for the process to be postulated.

EXPERIMENTAL PROCEDURE

Twenty-eight crystalline salts were tested as indicated in table I. A known quantity (about 0.2 g) of the salt was placed into an aluminum planchet (having a 6-mm-deep, 12-mm-diam. cavity). A tungsten target X-ray tube was used for irradiation, the conditions being 250 kilovolts, 10 milliamperes, and 30-minute exposure at about 10 centimeters from the target. The dose was about 400 000 roentgens.

Within several minutes after irradiation, the sample was added with no agitation to 5.00 ± 0.05 cubic centimeters of developer at room temperature. This developer was a 3 normal ammonium hydroxide solution containing 4 percent sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), 4 percent nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), and 4 percent of ammonium chloride (NH_4Cl) as a buffer. During the development process the soluble salts gradually dissolved while the insoluble ones did not. For the irradiated salts that were developable a metallic deposit was observed on the bottom of the beaker within 15 minutes after the start of development. On continued development for most of these cases, effervescence ensued while the metal continued to deposit as a fine black powder. Also, in some cases an adherent metallic mirror formed on the beaker. The developing mixtures were allowed to sit overnight to make sure ample time was provided for development. Only mixtures in which metallic deposits were observed were further treated; these were filtered into weighed crucibles, washed, dried at 120°C , and weighed.

The precipitates were analyzed spectroscopically and by X-ray diffraction and found to be essentially nickel metal. Emission spectroscopy indicated phosphorus as a significant contaminant although no nickel phosphide phase was revealed by X-ray diffraction. Lesser impurities of silicon, iron, magnesium, and calcium were usually found to be present spectroscopically.

At least two irradiation runs were made for each of the salts. Unirradiated salts added to the developer gave no observable metallic deposits.

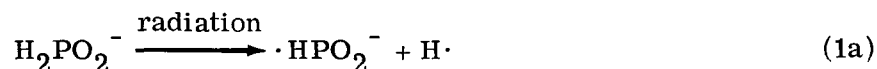
RESULTS

As seen in table I, six of the irradiated salts were found to be developable; that is, nickel was deposited when the irradiated salt was allowed to sit in the developer at room temperature, overnight. The six salts were nickel hypophosphite, sodium hypophosphite, ammonium hypophosphite, lithium hypophosphite, sodium phosphite, and nickel formate. The other salts listed in table I were not developable under the conditions used.

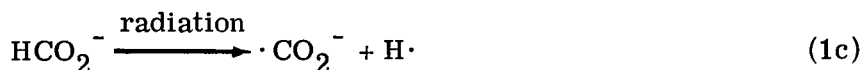
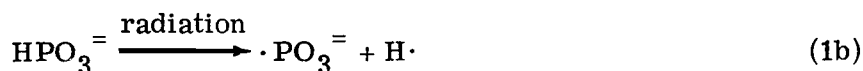
In general the quantity of nickel deposit (table I) roughly corresponded to that present in the developer used (0.051 g/5 cm^3 by gravimetric analysis). This was also true for irradiated nickel hypophosphite, even though additional nickel was available from the irradiated salt, itself. Nickel formate gave appreciably lower yields than the other developable salts.

DISCUSSION

Irradiation step. - Our results show that at least three types of salts are developable: hypophosphites, phosphites, and formates. Our approach to formulating the mechanism for the process was to determine what the irradiation of these salts have in common. Presumably, the irradiation of the hypophosphite ion (H_2PO_2^-) gives rise to a hydrogen atom ($\text{H}\cdot$) as well as the $\cdot\text{HPO}_2^-$ ion according to the following equation:



Electron Paramagnetic Resonance (EPR) studies have shown that a $\cdot\text{HPO}_2^-$ species is formed when hypophosphites are exposed to ionizing radiation. This species has been detected in γ -irradiated ammonium hypophosphites (ref. 2) as well as in γ -irradiated hypophosphites of magnesium, calcium, and sodium (ref. 3). At Lewis Research Center (unpublished work of John P. Jayne) the $\cdot\text{HPO}_2^-$ species has also been detected by EPR in the X-irradiated hypophosphites of ammonium, sodium, and barium. Similar reactions in which hydrogen atoms form are thought to take place when phosphites (HPO_3^-) and formates (HCO_2^-) are irradiated; that is,



The species $\cdot\text{PO}_3^{=}$ (ref. 4) and $\cdot\text{CO}_2^-$ (ref. 5) have been detected by EPR in irradiated sodium phosphite and sodium formate, respectively. In all three reactions (1a), (1b), and (1c) the hydrogen arises from the breaking of a covalent hydrogen bond.

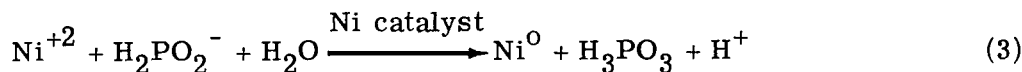
There appears to be no EPR evidence that the hydrogen atoms are held in the solid. However, our experimental results can be logically interpreted by postulating that hydrogen atoms are formed and then trapped in some way (perhaps chemically) in the solid salt. We believe that there is a common reducing species characteristic of all the irradiated salts which we found to be developable: namely, four hypophosphites, sodium phosphite, and nickel formate. Our data, however, are insufficient to ascertain the exact nature of the reducing species. For simplicity we will refer to this species as a trapped hydrogen atom.

Development. - We propose that when the irradiated salt is treated with developing solution, the trapped hydrogen atoms reduce small amounts of the divalent nickel ion (Ni^{+2}) in the developer to nickel metal (Ni^0), with the formation of hydrogen ions (H^+).



In reality, reaction (2) may involve three steps. The first would be the dissolution of the trapped hydrogen atom. This would be followed by the two-step reduction of the nickel ion to metallic nickel.

Of course, reaction (2) cannot account for the reduction of all the nickel present in the developer, as was found experimentally (table I). However, the micro amounts of nickel metal (nucleation sites) formed in reaction (2) would be expected to catalyze the well known electroless plating process: the reduction of nickel ion to nickel metal by hypophosphite using a metal catalyst (ref. 6). The equation would be:



Although according to reaction (3), the hypophosphite is converted to soluble phosphorus acid (H_3PO_3), the nickel metal obtained from such a process is known to be contaminated with up to 6 percent phosphorus (ref. 6). It should be noted that the nickel produced in

our development process also has a high phosphorus contamination. Furthermore, in earlier work of ours (refs. 7 and 8: the preparation of pure metals from their aqueous solution by radiation-induced reactions), nickel prepared in the presence of hypophosphite was also contaminated with phosphorus and the yields were higher than expected; this was all due to the occurrence of reaction (3).

Although reaction (3) is thermodynamically favored, it generally does not proceed at an appreciable rate at room temperature unless catalyzed. Moreover, reaction (3) is autocatalytic; the nickel produced in the reaction catalyzes still further reaction. Thus, large quantities of nickel can be produced by the catalytic action of an originally very small number of nickel nucleation sites.

The catalytic nature of the nickel produced in our present study is attested to by the effervescence which occurred during the development. The effervescence was indicative of hydrogen gas generation due to the catalyzed reduction of water by hypophosphite ion. We have further demonstrated that the nickel produced can be as effective as Raney nickel in the catalysis (ref. 1) of the Cannizzaro Reaction using formaldehyde (ref. 9). Thus, we believe that reaction (3) is the final step in our development process.

Comparison with the common photographic process. - Both the silver halide and our nickel hypophosphite systems depend on the radiative activation of a solid grain giving rise to a developable latent image. In the common photographic process, the activation involves decomposition of the silver halide by radiation to form metallic silver (ref. 10). The micro amounts of silver formed can catalyze the reduction of additional silver halide by the developer to form a visible silver image. In contrast, the activation step in the nickel system is believed to involve the formation of a trapped hydrogen atom. The development in this nickel system is more complex than that in the silver halide system in the sense that it involves two sequential steps even though a single developer is used. First, a relatively small number of nickel ions in the developer are reduced by the hydrogen atoms trapped in the grain to form micro amounts of catalytically active nickel. Second, this active nickel then promotes a further reaction in the developer resulting in the deposition of additional nickel metal. This second step of development produces a visible image. It is apparent that nickel need not be present in the original sensitive emulsion even though the final image is one of nickel metal.

Nondevelopable hypophosphites. - Our results (table I) show that several hypophosphites, for example, $\text{Ba}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$, are nondevelopable. EPR has shown that the $\cdot\text{HPO}_2^-$ which is present in developable hypophosphites is also present in the nondevelopable X-irradiated $\text{Ba}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$; thus, rupture of the phosphorus-hydrogen bond although necessary is not sufficient to produce a developable salt. In an auxiliary experiment (unpublished) the barium ion was found to prevent the development of irradiated sodium hypophosphite. Apparently the barium ion inhibits either step (2) or step (3) of the nickel forming process. At this time the cause of inhibition cannot be established.

The reason for some of the other irradiated hypophosphites being nondevelopable is more apparent. For instance, in the case of ferric hypophosphite, the following reaction is very likely to occur:



This could lead to insufficient hydrogen atoms for reaction (2) to occur. Similar reasoning can be extended to the undevelopable nature of irradiated lead hypophosphite; the lead ion could be reduced to metallic lead, thus again decreasing the hydrogen atom concentration. Any factor that interferes with any of the three steps of the process will inhibit the process.

Formates. - Our results with formates show that irradiated nickel formate is developable, whereas sodium formate is nondevelopable. Nevertheless, irradiation of sodium formate does form $\cdot\text{CO}_2^-$ ions (ref. 5) and presumably hydrogen atoms. The explanation for the nondevelopable nature of sodium formate may lie in the inability of the lattice to trap hydrogen atoms.

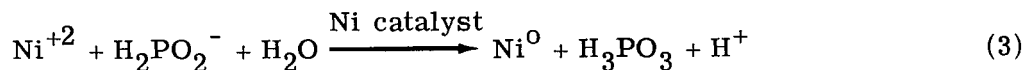
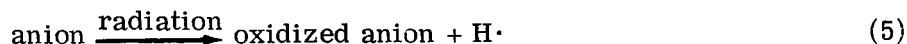
Alkali halides. - Trapped electrons (color centers) are present in irradiated alkali halides. Formation of trapped electrons instead of atomic hydrogen could logically represent the activation step in a developable system; nevertheless, irradiated alkali halides are found to be nondevelopable (table I). We suggest that, on exposure to the developer, the initial formation of active nickel does not occur due to a very rapid annihilation of electrons by oxidizing centers also produced during irradiation.

Other potentially developable irradiated compounds. - Our data indicate that some X-irradiated hypophosphites, phosphites, and formates can be developed. Apparently, the important thing in common to all three groups is a covalent hydrogen bond. Thus (solid) compounds, such as borohydrides, ortho arsenites, phosphonites, and organic compounds, in general, merit investigation. But, because the hydrogen bond itself must be sensitive to radiation, not every organic compound is a likely candidate. However, some hydrogen bonds may be quite sensitive to radiation; compounds containing such hydrogen bonds may even respond to visible light. Under such circumstances, we would indeed have a developable photographic system sensitive to visible light.

Finally, mention should be made of compounds which may not merit future study with nickel hypophosphite developer. These include salts of barium and iron because the cations involved appear to inhibit the development process.

RESUMÉ OF RESULTS

Six salts were found to be X-ray sensitive; that is, the irradiated salts would cause precipitation of nickel metal when treated with a nickel hypophosphite solution. The salts were: nickel hypophosphite, sodium hypophosphite, ammonium hypophosphite, lithium hypophosphite, sodium phosphite, and nickel formate. The process involves three reaction steps. The mechanism for the process is based on the postulate that trapped hydrogen atoms are formed during the irradiation step.



The first reaction depicts the irradiation process and the last two occur in a single development solution.

The process is similar in several respects to the common photographic process, in that irradiation produces a developable latent image. Even though the final image is nickel metal, the nickel ion need not be present in the irradiated emulsion or sample. Speculation leads to the existence of many more types of developable irradiated compounds, some of which may even be sensitive to visible light.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 24, 1971,
114-03.

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TABLE I. - YIELDS OF NICKEL OBTAINED BY DEVELOPMENT OF
VARIOUS IRRADIATED SALTS

[Sample: about 0.2 g
Irradiation: tungsten target X-ray tube, 250 kV, 10 mA, 30 min, 400 000 R
Developer: 3 N NH_4OH , 4% $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, 4% $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 4% NH_4Cl
Development: 5 cm^3 developer, sitting overnight, no agitation]

Compound	Formula	Purity	Yield of deposit, g
Nickel hypophosphite	$\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$	a	0.0439±0.003
Sodium hypophosphite	$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	b	.0542±0.0002
Ammonium hypophosphite	$\text{NH}_4\text{H}_2\text{PO}_2$	a	.0540±0.0005
Lithium hypophosphite	LiH_2PO_2	a	.0533±0.0004
Sodium phosphite	$\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$	c	.0408±0.006
Nickel formate	$\text{Ni}(\text{CHO}_2)_2 \cdot 2\text{H}_2\text{O}$	b	.0158±0.008
Barium hypophosphite	$\text{Ba}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$	b	0
Lead hypophosphite	$\text{Pb}(\text{H}_2\text{PO}_2)_2$	a	0 ^d
Ferric hypophosphite	$\text{Fe}(\text{H}_2\text{PO}_2)_3$	↓	0
Cobalt hypophosphite	$\text{Co}(\text{H}_2\text{PO}_2)_2$	↓	↓
Guanadine hypophosphite	$\text{C}(\text{NH}_2)_3\text{H}_2\text{PO}_2 \cdot 2\text{H}_2\text{O}$	↓	↓
Nickel oxalate	$\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	c	↓
Nickel acetate	$\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$	c	↓
Nickel acetylacetonate	$\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2$	b	↓
Nickel iodide	$\text{NiI}_2 \cdot 6\text{H}_2\text{O}$	b	↓
Potassium nickel cyanide	$\text{K}_2\text{Ni}(\text{CN})_4$	b	↓
Potassium iodide	KI	c	↓
Sodium bromide	NaBr	↓	↓
Sodium chloride	NaCl	↓	↓
Lithium fluoride	LiF	↓	↓
Magnesium oxide	MgO	↓	↓
Sodium formate	NaCHO_2	a	↓
Sodium sulfite	Na_2SO_3	c	↓
Sodium metabisulfite	$\text{Na}_2\text{S}_2\text{O}_5$	↓	↓
Sodium thiosulfate	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	↓	↓
Potassium oxalate	$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	↓	↓
Potassium thiocyanate	KCNS	↓	↓
Calcium dihydrogen phosphate	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	↓	↓

^aPrepared from reagent grade materials by one of the authors.

^bTechnical grade, best commercially available.

^cEither reagent, certified A.C.S., or C.P. grade.

^dOut of about 10 samples of $\text{Pb}(\text{H}_2\text{PO}_2)_2$ run, each of two gave what appeared to be a fleck of metal. These two results have been ignored.



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